The nature of rest silanol groups on the surfaces of silica based solid phase extraction materials

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Abstract. Chemically bonded solid phase materials are very important in separation chemistry. The chemically modified silica gel contains rest silanol groups that can affect the retention properties when they are used for separation of compounds. Some commercially available solid phase extraction (SPE) materials based on silica gel were analysed for rest silanol groups by near infrared spectroscopy. The combination frequency of the water molecules in the 5500- 5000 cm^{-1} region was used in identifying the nature of water molecules on the surface and the information was used to identify the types of silanol groups on the surface. Second derivative technique was employed in the detailed analysis.

Nine different SPE materials including C18, C8, C_6H_5, NH_2, OH, CN, SiOH, SA (SCX) and SB (SAX) were examined by near infrared spectroscopy for rest silanol groups. The results show that the non-polar and polar stationary phases contain vicinal silanol groups and the ion exchange solid phase materials contain free, vicinal and geminal silanol groups.

Introduction

Solid phase extraction (SPE) columns are important tools of an analytical chemist in pre-concentrating analyte from solutions containing the analyte. The separation is carried out by passing the solution containing the component of interest through a column containing a suitable SPE material. When suitable SPE material used, the separation is based on the fact that the solid phase has greater affinity to the solute or components a chemist wants to separate from the solution matrix. This fact helps a chemist to pre-concentrate either analyte from a solution matrix (isolation) or get rid of unwanted components (interference retention) in the solution matrix so that the filtrate is free from interfering components in the determination of the analyte. When the retained components on the SPE material are of interest then the components are eluted from the stationary SPE material using a suitable eluent (elution). Solid phase extraction is very widely used in isolating the analyte of interest from a variety of samples such as urine, blood serum, water etc. The mechanism of interaction of the components in the solution matrix and the solid stationary phase includes non polar, polar interactions, van der Waals interactions etc.

The columns used in solid phase extraction technology contain materials that are prepared from base materials. One of the important materials used as the base in preparing such materials is silica gel. It can be prepared by using different chemical reactions. One of the reactions is the condensation polymerisation of silicic acid. During the production, colloidal silica gel particles containing silanol groups on the surface are formed. On drying, several of the colloidal particles cohere and form particles with surface OH groups. The surface hydroxyl groups are polarised due to hydrogen bondings and the silanol groups exhibit different degrees of acidity [1,2]. The acidic nature of the silanol groups are responsible for the adsorption properties of silica gel and used in the separation of polar compounds. The OH groups of the silica gel particles can be chemically modified to produce materials that are suitable for separation science.

The modification of silica gel surface is carried out by using chemical reactions with chlorosilanes. The preparation of materials containing different surface functionalities is shown by a chemical reaction in Fig. 1. The reactions with chlorosilanes do not lead to the complete conversion of all the silanol groups. Some silanol groups may remain on the surface and materials produced by these reactions may have some unwanted characteristics in a chromatographic separation. The details regarding the silanol groups can be found elsewhere [3]. Effect of residual silanol groups in different aspects of separation science can be found in the references [4-8].

The rest silanol groups can be deactivated by chemical reactions called "end capping" where chlorosilanes with small alkyl groups are used to replace the hydrogens from these unwanted silanol groups (Fig. 1). The end capping reaction was almost effective in replacing most of the hydrogens in the rest silanol groups. However, a total derivatization of silanol groups seems not possible.

Christy has recently published a series of articles relating to silica gel and shown that the characteristics of silanol groups can be shown by Near infrared spectroscopy in combination with second derivative techniques [9-12]. The approach provided a way to distinguish between adsorption of water by hydrogen boned vicinal groups, geminal and free silanol groups on the surface. The adsorption of water molecules by a dry silica gel sample indicated by an absorption in the region 5600-5000 cm^{-1}. This absorption arises from the combination absorption of the OH stretching and bending fundamentals of the water molecules. This peak composed of three bands having maximum at 5314, 5270 and 5119 cm^{-1}. The first two bands are due to the OH groups of water molecules hydrogen bonded to free silanol groups, OH groups of water molecules hydrogen bonded to vicinal silanol groups on the surface respectively. The water molecules attached to geminal silanol groups absorb at a frequency slightly red shifted from 5270 cm^{-1}(5265 cm^{-1}) [11]. These absorptions are indicated in Fig. 2

The aim of this article is to show how near infrared spectroscopy can be used in analysing SPE materials for rest silanol groups and characterise their nature.

Experimental

Materials and preparation of the samples. Chromabond standard development kit containing 11 different solid phase extraction materials including C18, C8, C_6H_5, NH_2, OH, CN, SiOH, SA (SCX), SB (SAX) was bought from Machery Nagel. The particles of the SPE materials had a size of 45 μm and a pore size of 60 Å. According to the manufacturer, most of the phase materials were not end-capped. The SPE materials were packed in 3 ml plastic syringes and had a mass of 500 mg each. A total of nine columns containing one each of the above mentioned phases were selected for near infrared analysis

A ceramic heater (BA electric Bunsen from Electrothermal, UK) controlled by an external power supply was used in heating the samples. The temperature of the sample was measured by using a digital thermometer with a K type thermocouple (Clasohlson, UK). A powerful vacuum pump (Edwards, UK) was used in the evacuation of the samples.

Near infrared (NIR) measurements. The near infrared measurements were made using a PerkinElmer Spectrum One NTS FT-NIR spectrometer (Perkin Elmer Ltd, UK) equipped with a PerkinElmer transflectance accessory and deuterated triglycine sulphate detector. Each of the columns containing the sample was cut open and the content was placed in a glass vial with screw cap containing an air tight septum. The vial was then placed directly on the crystal of the transflectance accessory and the near infrared spectrum of the sample was measured in the region 10,000–4000 cm^{-1} at a resolution of 16 cm^{-1}. A total of 30 scans were made each time. The glass vial was then evacuated at 160 ^oC for 30 minutes, cooled and a new NIR spectrum was acquired using the same parameters. The reflectance spectra of the samples so obtained were converted to log (1/*R*) format and saved. The spectra of the samples in log(1/R) format were derivated twice and saved. These spectra were used in the detailed analysis of the SPE materials.

Results and discussion

The near infrared band assignments for an SPE material containing an aliphatic chain as the reverse phase is given in Table 1. The second derivative profiles of the near infrared spectra of the silica (OH) and C18 SPE materials from the extraction columns are given in the regions 7450-6950 and 5500-5050 cm^{-1} in Fig. 3 a and b respectively. The OH 1^{st} overtone region of the spectra clearly shows strong absorptions at 5270 cm^{-1} which confirms the presence of vicinal silanol groups on the surface of C18 SPE material. This absorption is stronger than the water molecules hydrogen bonded to vicinal groups in silica gel suggesting the formation of new silanol groups during the derivatisation reaction which leads to hydrogen bond formation with free silanol groups causing an increase in the vicinal silanol groups.

Near infrared spectra and the second derivative profiles of C18 and anionic exchange material SA are shown in Fig. 4a and b respectively. The Fig. 4a displays

the NIR spectra and their second derivative profiles of the C18 SPE material from the cartridge and the NIR spectra obtained after drying the material at 160 ^{o}C. A closer look at the spectra and comparison reveal that the C18 material has only hydrogen bonded vicinal groups in the matrix which again hydrogen bond to water

Table 1 Near Infrared band assignments for C18 solid phase extraction material

Peak (cm^{-1})	**Band assignment**
9200-7600	CH second overtone and OH combination
7316	Overtone-OH stretchings-free silanol groups
7225- 6860	Silanol groups hydrogen bonded to water molecules Water molecules hydrogen bonded to silanol groups, water molecules hydrogen bonded to other water molecules
5950-5300	First CH overtone
5311	Combination band OH stretching and bending water molecules hydrogen bonded to free silanol groups
5270 (5265)	Water molecules hydrogen bonded to vicinal silanol groups (geminal silanol groups)
5119	Water molecules hydrogen bonded to silanol groups
4579	Combination band OH stretching and siloxane (Si-O-SI) bending
4500-4400	Combination band silanol OH stretching (hydrogen bonded to water molecules)and siloxane (Si-O-Si) bending

molecules. A similar look at the anionic exchange material SA shows that the material has both free and hydrogen bonded silanol groups on the surface. The combination frequency of the water molecules appear at 5265 cm^{-1} indicating that a part of the hydrogen bonded silanol groups are germinal silanol groups.

Second derivative profiles of the NIR spectra of the SA and SB materials are shown in Fig. 5 for comparison. The figure shows clearly the presence of free silanol groups and hydrogen bonded silanol groups in these materials. The anion exchange material has more hydrogen bonded silanol groups compared to cation exchange SPE material. The OH combination frequency of the water molecules hydrogen bonded to silanol groups appear around 5263 cm $^{-1}$. This indicates the presence of geminal silanol groups together with vicinal silanol groups on the surfaces of the anion (SA) and cation (SB) exchange SPE materials.

Observations similar to C18 material were made with the SPE materials C8, CH, PH, CN and NH_2 phases.

Conclusion

The use of near infrared spectroscopy and second derivative techniques in identifying rest silanol groups on chemically modified solid phase materials based on silica gel has been clearly demonstrated for the first time in this paper. A quick qualitative characterization of the silanol groups is possible from the second derivative spectrum of an SPE material.

The rest silanol groups on solid phases chemically modified to contain non polar and polar functional groups on the surface are mostly vicinal and germinal silanol groups. The rest silanol groups on the solid phases modified to contain ionic exchange properties are free, vicinal and germinal silanol groups.

The rest silanol groups and their nature in these materials can influence the separation of a mixture. One should be aware and take into account the effects these groups can cause in a chromatographic separation.

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Fig. 1

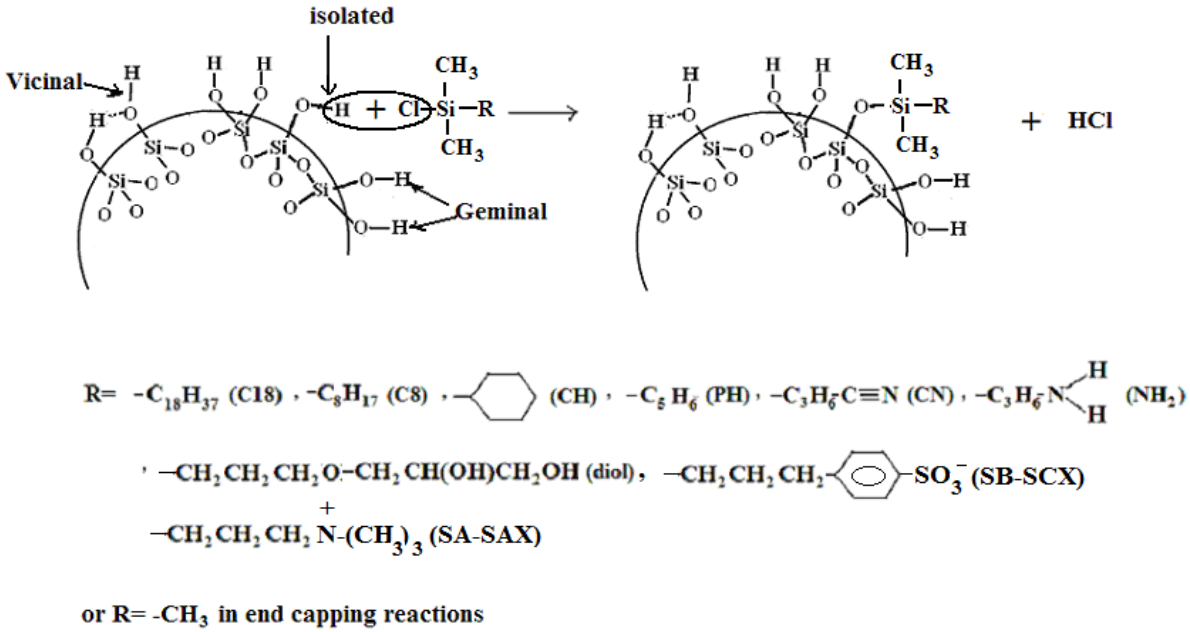

Fig. 1. A figure showing how the silanol groups are derivatised by reactions with chlorosilanes.

Fig. 2

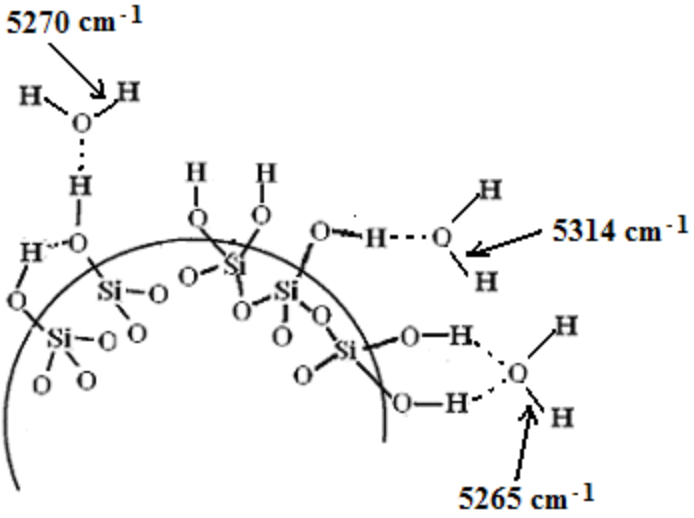

Fig. 2. The combination frequency of O-H stretching and bending absorptions of water molecules hydrogen bonded to different surface silanol groups

Fig. 3

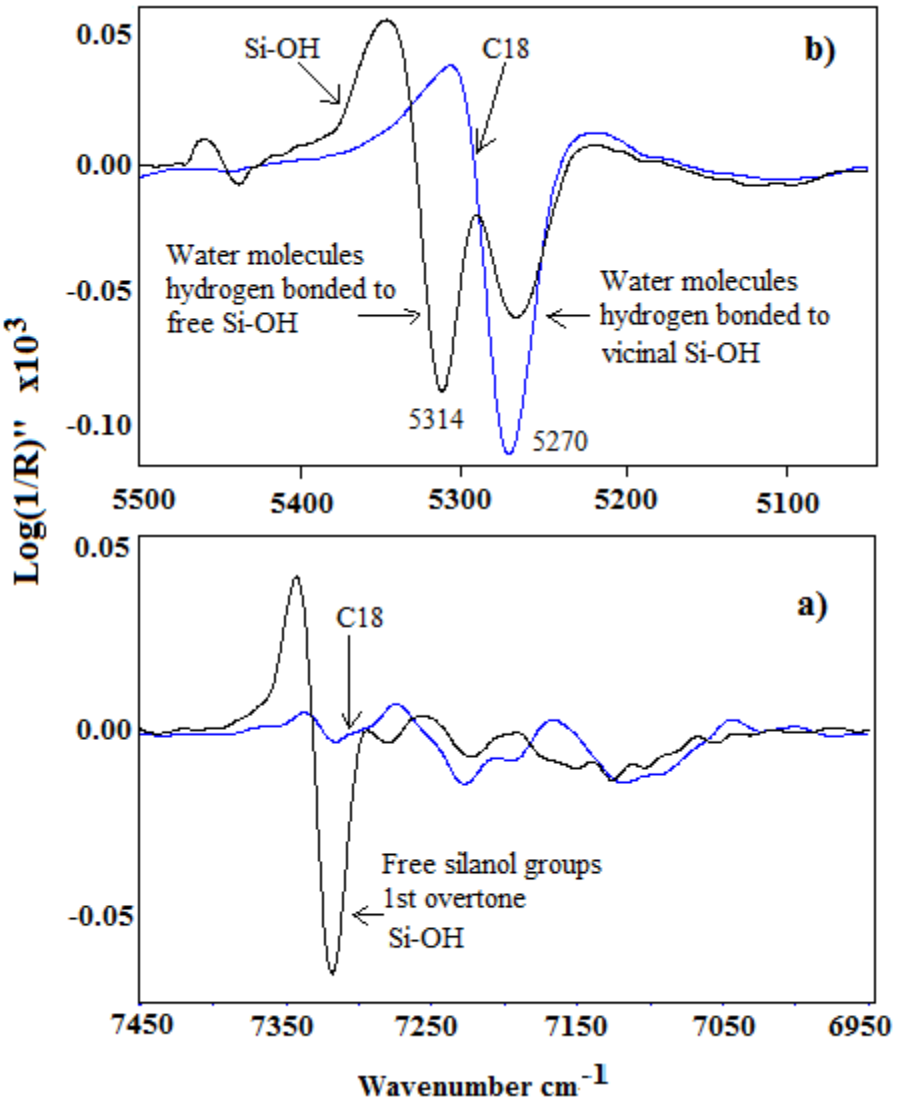

Fig. 3. Second derivative profiles of the NIR spectra of silica gel and C18 SPE material

Fig. 4

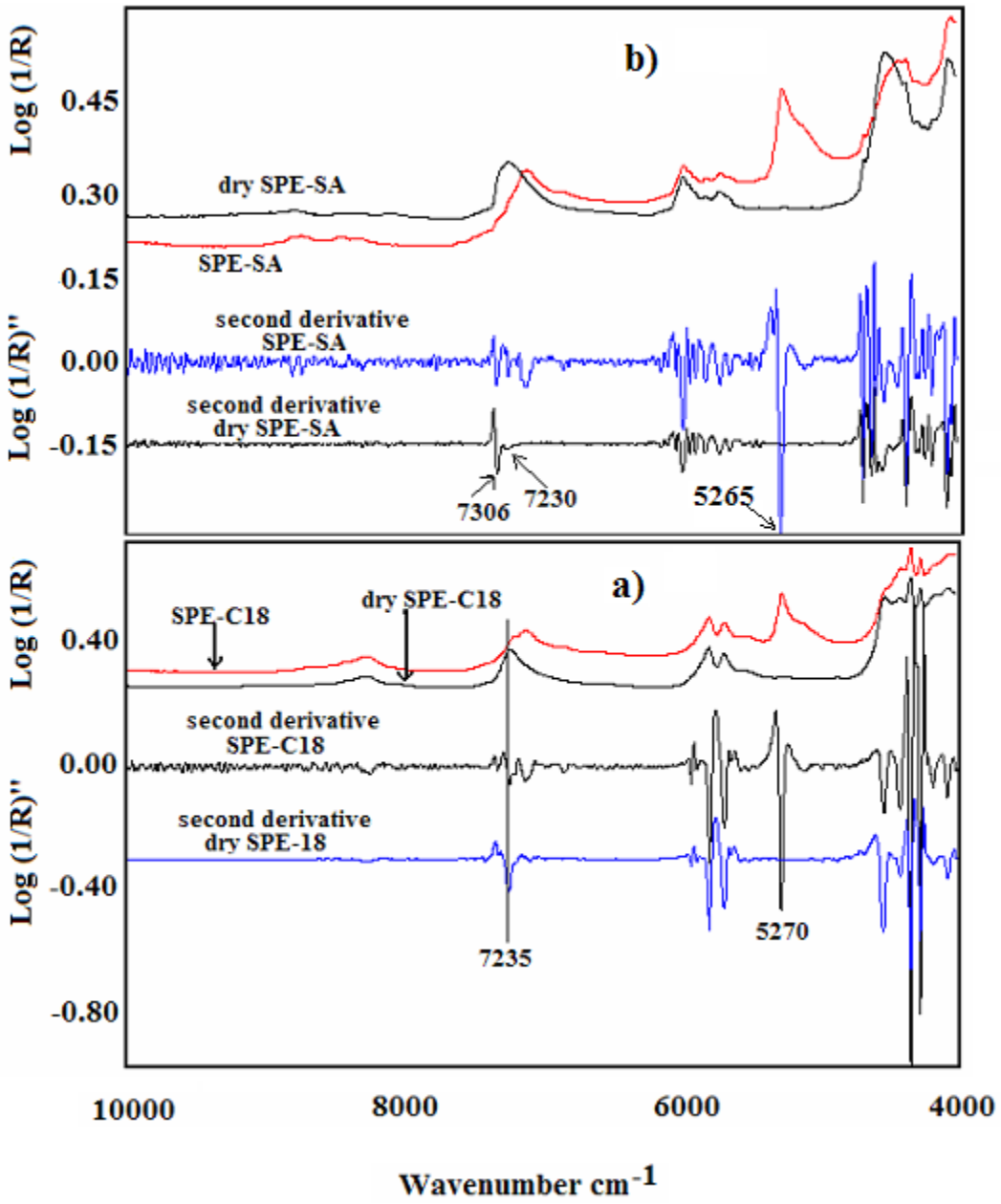

Fig. 4. Near infrared spectra and their second derivative profiles of C18 and anionic exchange (SA) SPE materials a) for C18 SPE material from the cartridge and after drying at 160 $_{o}$C b) for SA-SPE material from the cartridge and after drying at 160 $_{o}$C. The absorbance spectra and the second derivative profiles are scale adjusted for clarity

Fig. 5

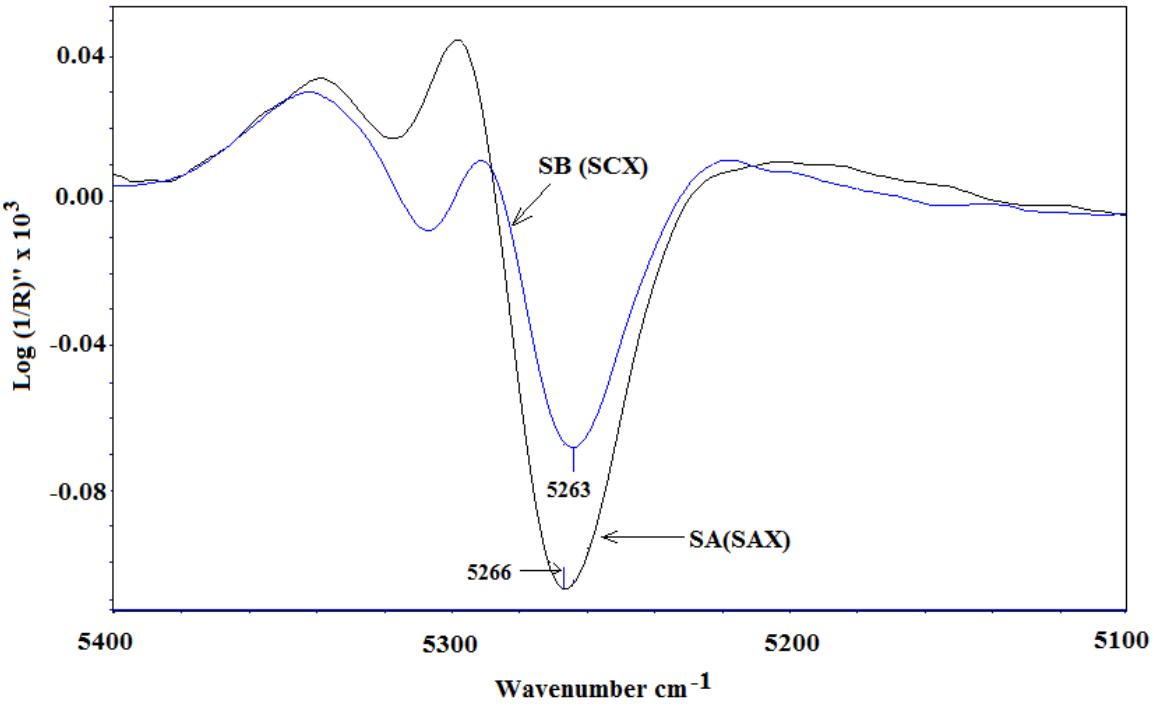

Fig. 5. Second derivative profiles of the NIR spectra of anion (SA) and cation (SB) SPE materials from the cartridges in the region 5400-5100 cm-1